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<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; border: none;"> <p>(21) International Application Number: PCT/US93/12361</p> <p>(22) International Filing Date: 17 December 1993 (17.12.93)</p> <p>(30) Priority Data: 07/993,179 18 December 1992 (18.12.92) US</p> <p>(71) Applicant: CHEVRON RESEARCH AND TECHNOLOGY COMPANY [US/US]; A division of Chevron U.S.A. Inc., P.O. Box 7141, San Francisco, CA 94120-7141 (US).</p> <p>(72) Inventor: CHERPECK, Richard, E.; 8962 Cypress Avenue, Cotati, CA 94931 (US).</p> <p>(74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).</p> </td> <td style="width: 50%; vertical-align: top; border: none;"> <p>(81) Designated States: AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> </td> </tr> </table>			<p>(21) International Application Number: PCT/US93/12361</p> <p>(22) International Filing Date: 17 December 1993 (17.12.93)</p> <p>(30) Priority Data: 07/993,179 18 December 1992 (18.12.92) US</p> <p>(71) Applicant: CHEVRON RESEARCH AND TECHNOLOGY COMPANY [US/US]; A division of Chevron U.S.A. Inc., P.O. Box 7141, San Francisco, CA 94120-7141 (US).</p> <p>(72) Inventor: CHERPECK, Richard, E.; 8962 Cypress Avenue, Cotati, CA 94931 (US).</p> <p>(74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).</p>	<p>(81) Designated States: AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
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<p>(54) Title: POLY(OXYALKYLENE) HYDROXYAROMATIC ESTERS AND FUEL COMPOSITIONS CONTAINING THE SAME</p> <div style="text-align: center; margin: 10px 0;"> $R_1 - \text{C}_6\text{H}_3(\text{OH})(R_2) - (\text{CH}_2)_x - \text{C}(=\text{O}) - \text{O} - \text{CH}(R_3) - \text{CH}(R_4) - \text{O} - R_5 \quad (I)$ </div> <div style="text-align: center; margin: 10px 0;"> $-\text{C}(=\text{O}) - R_6 \quad (1)$ </div> <div style="text-align: center; margin: 10px 0;"> $-\text{C}(=\text{O}) - (\text{CH}_2)_y - \text{C}_6\text{H}_3(\text{OH})(R_7)(R_8) \quad (2)$ </div> <p>(57) Abstract</p> <p>Poly(oxyalkylene) hydroxyaromatic esters having formula (I), or a fuel-soluble salt thereof, where R₁ and R₂ are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; R₃ and R₄ are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R₅ is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group having formula (1) or (2), wherein R₆ is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms; R₇ and R₈ are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; n is an integer from 5 to 100; and x and y are each independently an integer from 0 to 10. The poly(oxyalkylene) hydroxyaromatic esters of formula (I) are useful as fuel additives for the prevention and control of engine deposits.</p>				

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01 POLY(OXYALKYLENE) HYDROXYAROMATIC ESTERS
02 AND FUEL COMPOSITIONS CONTAINING THE SAME

03

04

BACKGROUND OF THE INVENTION

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06 Field of the Invention

07

08 This invention relates to novel hydroxyaromatic compounds.
09 More particularly, this invention relates to novel
10 poly(oxyalkylene) hydroxyaromatic esters and their use in
11 fuel compositions to prevent and control engine deposits.

12

13 Description of the Related Art

14

15 It is well known that automobile engines tend to form
16 deposits on the surface of engine components, such as
17 carburetor ports, throttle bodies, fuel injectors, intake
18 ports and intake valves, due to the oxidation and
19 polymerization of hydrocarbon fuel. These deposits, even
20 when present in relatively minor amounts, often cause
21 noticeable driveability problems, such as stalling and poor
22 acceleration. Moreover, engine deposits can significantly
23 increase an automobile's fuel consumption and production of
24 exhaust pollutants. Therefore, the development of effective
25 fuel detergents or "deposit control" additives to prevent or
26 control such deposits is of considerable importance and
27 numerous such materials are known in the art.

28

29 For example, aliphatic hydrocarbon-substituted phenols are
30 known to reduce engine deposits when used in fuel
31 compositions. U.S. Patent No. 3,849,085, issued November
32 19, 1974 to Kreuz et al., discloses a motor fuel composition
33 comprising a mixture of hydrocarbons in the gasoline boiling
34 range containing about 0.01 to 0.25 volume percent of a high
35 molecular weight aliphatic hydrocarbon-substituted phenol in

01 which the aliphatic hydrocarbon radical has an average
02 molecular weight in the range of about 500 to 3,500. This
03 patent teaches that gasoline compositions containing minor
04 amount of an aliphatic hydrocarbon-substituted phenol not
05 only prevent or inhibit the formation of intake valve and
06 port deposits in a gasoline engine, but also enhance the
07 performance of the fuel composition in engines designed to
08 operate at higher operating temperatures with a minimum of
09 decomposition and deposit formation in the manifold of the
10 engine.

11

12 Similarly, U.S. Patent No. 4,134,846, issued January 16,
13 1979 to Machleder et al., discloses a fuel additive
14 composition comprising a mixture of (1) the reaction product
15 of an aliphatic hydrocarbon-substituted phenol,
16 epichlorohydrin and a primary or secondary mono- or
17 polyamine, and (2) a polyalkylene phenol. This patent
18 teaches that such compositions show excellent carburetor,
19 induction system and combustion chamber detergency and, in
20 addition, provide effective rust inhibition when used in
21 hydrocarbon fuels at low concentrations.

22

23 Fuel additives containing a poly(oxyalkylene) moiety are
24 also known in the art. For example, U.S. Patent No.
25 4,191,537, issued March 4, 1980 to R. A. Lewis et al.,
26 discloses a fuel composition comprising a major portion of
27 hydrocarbons boiling in the gasoline range and from 30 to
28 2000 ppm of a hydrocarbyl poly(oxyalkylene) aminocarbamate
29 having a molecular weight from about 600 to 10,000, and at
30 least one basic nitrogen atom. The hydrocarbyl
31 poly(oxyalkylene) moiety is composed of oxyalkylene units
32 selected from 2 to 5 carbon oxyalkylene units. These fuel
33 compositions are taught to maintain the cleanliness of
34 intake systems without contributing to combustion chamber
35 deposits.

-3-

01 Aromatic compounds containing a poly(oxyalkylene) moiety are
02 also known in the art. For example, the above-mentioned
03 U.S. Patent No. 4,191,537, discloses alkylphenyl
04 poly(oxyalkylene) polymers which are useful as intermediates
05 in the preparation of alkylphenyl poly(oxyalkylene)
06 aminocarbamates.

07

08 Additionally, hydroxyaromatic compounds containing a
09 poly(oxyalkylene) moiety are known in the art. For example,
10 U.S. Patent No. 4,952,732, issued August 28, 1990 to G. P.
11 Speranza et al., discloses Mannich condensates prepared from
12 a phenol, formaldehyde and an alkylamine containing propoxy
13 groups and, optionally, ethoxy groups. These Mannich
14 condensates are taught to be useful as corrosion inhibitors,
15 water repellent agents, paint adhesion promoters, and also
16 as intermediates for preparing surfactants, and pololys
17 finding use in the manufacture of polyurethane foam.

18

19 It has now been discovered that certain hydroxyaromatic
20 esters having a poly(oxyalkylene) "tail" provide excellent
21 control of engine deposits, especially intake valve
22 deposits, when employed as fuel additives in fuel
23 compositions. Moreover, these poly(oxyalkylene)
24 hydroxyaromatic esters have been found to produce fewer
25 combustion chamber deposits than known aliphatic
26 hydrocarbon-substituted phenolic fuel additives.

27

28

29

SUMMARY OF THE INVENTION

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31 The present invention provides novel poly(oxyalkylene)
32 hydroxyaromatic esters which are useful as fuel additives
33 for the prevention and control of engine deposits,
34 particularly intake valve deposits.

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-4-

01 The poly(oxyalkylene) hydroxyaromatic esters of the present
 02 invention have the formula:

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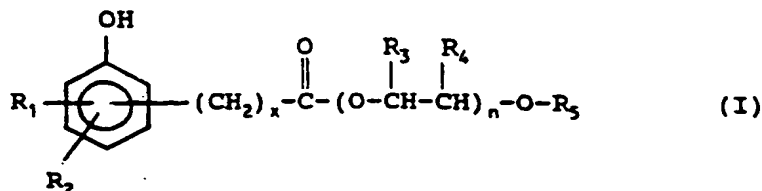
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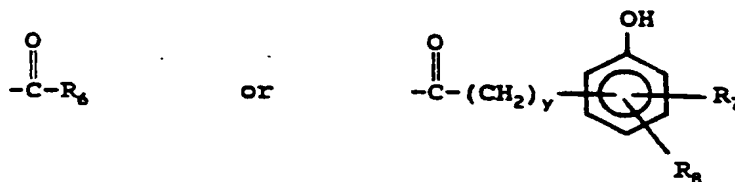
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or a fuel-soluble salt thereof; wherein R_1 and R_2 are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; R_3 and R_4 are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R_5 is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of the formula:



wherein R_6 is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms; R_7 and R_8 are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; n is an integer from 5 to 100; and x and y are each independently an integer from 0 to 10.

The present invention further provides a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and an effective deposit-controlling amount of a hydroxyaromatic poly(oxyalkylene)

01 ester of the present invention.

02

03 The present invention additionally provides a fuel
04 concentrate comprising an inert stable oleophilic organic
05 solvent boiling in the range of from about 150°F to 400°F
06 and from about 10 to 70 weight percent of a hydroxyaromatic
07 poly(oxyalkylene) ester of the present invention.

08

09 Among other factors, the present invention is based on the
10 surprising discovery that certain poly(oxyalkylene)
11 hydroxyaromatic esters, when employed as fuel additives in
12 fuel compositions, provide excellent control of engine
13 deposits, especially on intake valves, and produce fewer
14 combustion chamber deposits than known aliphatic
15 hydrocarbon-substituted phenolic fuel additives.

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18 DETAILED DESCRIPTION OF THE INVENTION

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20 The fuel additives provided by the present invention have
21 the general formula:

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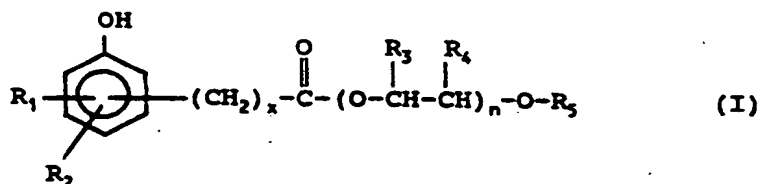
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30 or a fuel-soluble salt thereof; wherein R_1 , R_2 , R_3 , R_4 , R_5 , n
31 and x are as defined hereinabove.

32

33 Preferably, R_1 is hydrogen, hydroxy, or lower alkyl having 1
34 to 4 carbon atoms. More preferably, R_1 is hydrogen or
35 hydroxy. Most preferably, R_1 is hydrogen.



-6-

01 R_2 is preferably hydrogen.

02

03 Preferably, one of R_3 and R_4 is lower alkyl having 1 to 3
04 carbon atoms and the other is hydrogen. More preferably,
05 one of R_3 and R_4 is methyl or ethyl and the other is
06 hydrogen. Most preferably, one of R_3 and R_4 is ethyl and
07 the other is hydrogen.

08

09 R_5 is preferably hydrogen, alkyl having 2 to 22 carbon
10 atoms, or alkylphenyl having an alkyl group containing 2 to
11 24 carbon atoms. More preferably, R_5 is hydrogen, alkyl
12 having 4 to 12 carbon atoms or alkylphenyl having an alkyl
13 group containing 4 to 12 carbon atoms. Most preferably, R_5
14 is alkylphenyl having an alkyl group containing 4 to 12
15 carbon atoms.

16

17 R_6 is preferably alkyl having 4 to 12 carbon atoms.

18

19 Preferably, R_7 is hydrogen, hydroxy, or lower alkyl having 1
20 to 4 carbon atoms. More preferably, R_7 is hydrogen or
21 hydroxy. Most preferably, R_7 is hydrogen.

22

23 R_8 is preferably hydrogen.

24

25 Preferably, n is an integer from 10 to 50. More preferably,
26 n is an integer from 15 to 30. Preferably, x is an integer
27 from 0 to 2. More preferably, x is 0. Preferably, y is an
28 integer from 0 to 2. More preferably, y is 0.

29

30 A preferred group of poly(oxyalkylene) hydroxyaromatic
31 esters are those of formula I wherein R_1 is hydrogen,
32 hydroxy, or lower alkyl having 1 to 4 carbon atoms; R_2 is
33 hydrogen; one of R_3 and R_4 is hydrogen and the other is
34 methyl or ethyl; R_5 is hydrogen, alkyl having 2 to about 22
35 carbon atoms or alkylphenyl having an alkyl group containing

-7-

01 4 to about 24 carbon atoms; n is 15 to 30 and x is 0.

02

03 Another preferred group of poly(oxyalkylene) hydroxyaromatic
 04 esters are those of formula I wherein R_1 is hydrogen,
 05 hydroxy, or lower alkyl having 1 to 4 carbon atoms; R_2 is
 06 hydrogen; one of R_3 and R_4 is hydrogen and the other is
 07 methyl or ethyl; R_5 is hydrogen, alkyl having 2 to about 22
 08 carbon atoms or alkylphenyl having an alkyl group containing
 09 4 to about 24 carbon atoms; n is 15 to 30 and x is 1 or 2.

10

11 A more preferred group of poly(oxyalkylene) hydroxyaromatic
 12 esters are those of formula I wherein R_1 is hydrogen or
 13 hydroxy; R_2 is hydrogen; one of R_3 and R_4 is hydrogen and the
 14 other is methyl or ethyl; R_5 is hydrogen, alkyl having 4 to
 15 12 carbon atoms or alkylphenyl having an alkyl group
 16 containing 4 to 12 carbon atoms; n is 15 to 30; and x is 0.

17

18 A particularly preferred group of poly(oxyalkylene)
 19 hydroxyaromatic esters are those having the formula:

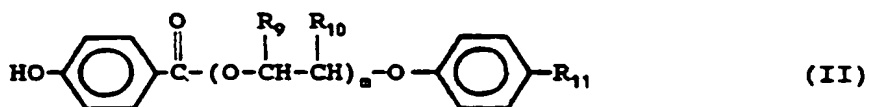
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25 wherein one of R_9 and R_{10} is methyl or ethyl and the other is
 26 hydrogen; R_{11} is an alkyl group having 4 to 12 carbon atoms;
 27 and m is an integer from 15 to 30.

28

29 It is especially preferred that the aromatic hydroxyl group
 30 or groups present in the poly(oxyalkylene) hydroxyaromatic
 31 esters of this invention be situated in a meta or para
 32 position relative to the poly(oxyalkylene) ester moiety.

33 When the aromatic moiety contains one hydroxyl group, it is
 34 particularly preferred that this hydroxyl group be in a para

35

01 position relative to the poly(oxyalkylene) ester moiety.

02

03 The poly(oxyalkylene) hydroxyaromatic esters of the present
04 invention will generally have a sufficient molecular weight
05 so as to be non-volatile at normal engine intake valve
06 operating temperatures (about 200-250°C). Typically, the
07 molecular weight of the poly(oxyalkylene) hydroxyaromatic
08 esters of this invention will range from about 600 to about
09 10,000, preferably from 1,000 to 3,000.

10

11 Generally, the poly(oxyalkylene) hydroxyaromatic esters of
12 this invention will contain an average of about 5 to about
13 100 oxyalkylene units; preferably, 10 to 50 oxyalkylene
14 units; more preferably, 15 to 30 oxyalkylene units.

15

16 Fuel-soluble salts of the poly(oxyalkylene) hydroxyaromatic
17 esters of the present invention are also contemplated to be
18 useful for preventing or controlling deposits. Such salts
19 include alkali metal, alkaline earth metal, ammonium,
20 substituted ammonium and sulfonium salts. Preferred metal
21 salts are the alkali metal salts, particularly the sodium
22 and potassium salts, and the substituted ammonium salts,
23 particularly tetraalkyl-substituted ammonium salts, such as
24 the tetrabutylammonium salts.

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01 Definitions

02

03 As used herein the following terms have the following
04 meanings unless expressly stated to the contrary.

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06 The term "alkyl" refers to both straight- and branched-chain
07 alkyl groups.

08

09 The term "lower alkyl" refers to alkyl groups having 1 to
10 about 6 carbon atoms and includes primary, secondary and
11 tertiary alkyl groups. Typical lower alkyl groups include,
12 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,
13 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

14

15 The term "lower alkoxy" refers to the group $-OR_a$ wherein R_a
16 is lower alkyl. Typical lower alkoxy groups include
17 methoxy, ethoxy, and the like.

18

19 The term "alkaryl" refers to the group:

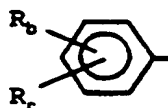
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25 wherein R_b and R_c are each independently hydrogen or an
26 alkyl group, with the proviso that both R_b and R_c are not
27 hydrogen. Typical alkaryl groups include, for example,
28 tolyl, xylyl, cumenyl, ethylphenyl, butylphenyl,
29 dibutylphenyl, hexylphenyl, octylphenyl, dioctylphenyl,
30 nonylphenyl, decylphenyl, didecylphenyl, dodecylphenyl,
31 hexadecylphenyl, octadecylphenyl, icosylphenyl,
32 tricontylphenyl and the like. The term "alkylphenyl" refers
33 to an alkaryl group of the above formula in which R_b is
34 alkyl and R_c is hydrogen.

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01 The term "aralkyl" refers to the group:

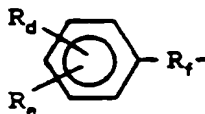
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07 wherein R_d and R_e are each independently hydrogen or an
 08 alkyl group; and R_f is an alkylene group. Typical alkaryl
 09 groups include, for example, benzyl, methylbenzyl,
 10 dimethylbenzyl, phenethyl, and the like.

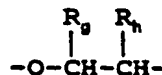
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12 The term "oxyalkylene unit" refers to an ether moiety having
 13 the general formula:

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18 wherein R_g and R_h are each independently hydrogen or lower
 19 alkyl groups.

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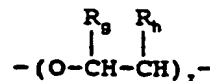
21 The term "poly(oxyalkylene)" refers to a polymer or oligomer
 22 having the general formula:

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27

28 wherein R_g and R_h are as defined above, and z is an integer
 29 greater than 1. When referring herein to the number of
 30 poly(oxyalkylene) units in a particular poly(oxyalkylene)
 31 compound, it is to be understood that this number refers to
 32 the average number of poly(oxyalkylene) units in such
 33 compounds unless expressly stated to the contrary.

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36

01 General Synthetic Procedures

02

03 The poly(oxyalkylene) hydroxyaromatic esters of this
 04 invention may be prepared by the following general methods
 05 and procedures. It should be appreciated that where typical
 06 or preferred process conditions (e.g. reaction temperatures,
 07 times, mole ratios of reactants, solvents, pressures, etc.)
 08 are given, other process conditions may also be used unless
 09 otherwise stated. Optimum reaction conditions may vary with
 10 the particular reactants or solvents used, but such
 11 conditions can be determined by one skilled in the art by
 12 routine optimization procedures.

13

14 The poly(oxyalkylene) hydroxyaromatic esters of the present
 15 invention having the formula:

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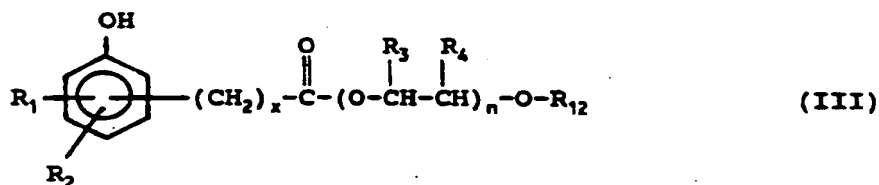
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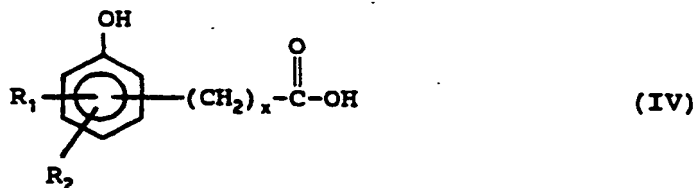
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wherein R_1 - R_4 , n and x are as defined above and R_{12} is an
 alkyl, phenyl, aralkyl or alkaryl group, may be prepared by
 esterifying a hydroxyaromatic carboxylic acid having the
 formula:



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01 wherein R_1 , R_2 , and x are as defined above, with a
 02 poly(oxyalkylene) alcohol having the formula:



07
 08 wherein R_3 , R_4 , R_{12} and n are as defined above, using
 09 conventional esterification reaction conditions.
 10

11 The hydroxyaromatic carboxylic acids of formula IV are
 12 either known compounds or can be prepared from known
 13 compounds by conventional procedures. Suitable
 14 hydroxyaromatic carboxylic acids for use as starting
 15 materials in this invention are 2-hydroxybenzoic acid, 3-
 16 hydroxybenzoic acid, 4-hydroxybenzoic acid, 3,4-
 17 dihydroxybenzoic acid, 3,4,5-trihydroxybenzoic acid, 3-
 18 hydroxy-4-methoxybenzoic acid, 4-hydroxy-3-methoxybenzoic
 19 acid, 3-t-butyl-4-hydroxybenzoic acid, 3,5-di-t-butyl-4-
 20 hydroxybenzoic acid, 4-hydroxyacetic acid, 3-(4-
 21 hydroxyphenyl)propionic acid and the like.
 22

23 The poly(oxyalkylene) alcohols of formula V may also be
 24 prepared by conventional procedures known in the art. Such
 25 procedures are taught, for example, in U.S. Patent Nos.
 26 2,782,240 and 2,841,479, which are incorporated herein by
 27 reference.
 28

29 Preferably, the poly(oxyalkylene) alcohols of formula V are
 30 prepared by contacting an alkoxide or phenoxide metal salt
 31 having the formula:
 32



-13-

01 wherein R_{12} is as defined above and M is a metal cation,
02 such as lithium, sodium, or potassium, with about 5 to about
03 100 molar equivalents of an alkylene oxide (an epoxide)
04 having the formula:

05

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(VII)

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wherein R_3 and R_4 are as defined above.

Generally, metal salt VI is prepared by contacting the corresponding hydroxy compound $R_{12}\text{OH}$ with a strong base, such as sodium hydride, potassium hydride, sodium amide and the like, in an inert solvent, such as toluene, xylene and the like, under substantially anhydrous conditions at a temperature in the range from about -10°C to about 120°C for about 0.25 to about 3 hours.

Metal salt VI is generally not isolated, but is reacted *in situ* with the alkylene oxide VII to provide, after neutralization, the poly(oxyalkylene) alcohol V. This polymerization reaction is typically conducted in a substantially anhydrous inert solvent at a temperature of about 30°C to about 150°C for about 2 to about 120 hours. Suitable solvents for this reaction, include toluene, xylene and the like. The reaction will generally be conducted at a pressure sufficient to contain the reactants and the solvent, preferably at atmospheric or ambient pressure.

The amount of alkylene oxide employed in this reaction will depend on the number of oxyalkylene units desired in the product. Typically, the molar ratio of alkylene oxide VII to metal salt VI will range from about 5:1 to about 100:1;

-14-

01 preferably, from 10:1 to 50:1, more preferably from 15:1 to
02 30:1.

03

04 Suitable alkylene oxides for use in the polymerization
05 reaction include, for example, ethylene oxide; propylene
06 oxide; butylene oxides, such as 1,2-butylene oxide (1,2-
07 epoxybutane) and 2,3-butylene oxide (2,3-epoxybutane);
08 pentylene oxides; hexylene oxides; octylene oxides and the
09 like. Preferred alkylene oxides are propylene oxide and
10 1,2-butylene oxide.

11

12 In the polymerization reaction, a single type of alkylene
13 oxide may be employed, e.g. propylene oxide, in which case
14 the product is a homopolymer, e.g. a poly(oxypropylene).
15 However, copolymers are equally satisfactory and random
16 copolymers are readily prepared by contacting the metal salt
17 VI with a mixture of alkylene oxides, such as a mixture of
18 propylene oxide and 1,2-butylene oxide, under polymerization
19 conditions. Copolymers containing blocks of oxyalkylene
20 units are also suitable for use in the present invention.
21 Block copolymers may be prepared by contacting the metal
22 salt VI with first one alkylene oxide, then others in any
23 order, or repetitively, under polymerization conditions.

24

25 The poly(oxyalkylene) alcohol V may also be prepared by
26 living or immortal polymerization as described by S. Inoue
27 and T. Aida in *Encyclopedia of Polymer Science and*
28 *Engineering*, Second Edition, Supplemental Volume, J. Wiley
29 and Sons, New York, pages 412-420 (1989). These procedures
30 are especially useful for preparing poly(oxyalkylene)
31 alcohols of formula V in which R_3 and R_4 are both alkyl
32 groups.

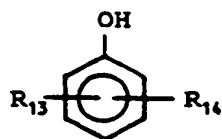
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34 As noted above, the alkoxide or phenoxide metal salt VI is

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01 generally derived from the corresponding hydroxy compound,
02 $R_{12}OH$. Preferred hydroxy compounds for use in this
03 invention include straight- or branched-chain aliphatic
04 alcohols having 1 to about 30 carbon atoms and phenols
05 having the formula:



(VIII)

12 wherein R_{13} and R_{14} are each independently hydrogen or an
13 alkyl group having 1 to about 30 carbon atoms.

14
15 Preferably, the straight- or branched-chain aliphatic
16 alcohols employed in this invention will contain 2 to about
17 22 carbon atoms, more preferably 4 to 12 carbon atoms.
18 Representative examples of straight- or branched-chain
19 aliphatic alcohols suitable for use in this invention
20 include, but are not limited to, n-butanol; isobutanol; sec-
21 butanol; t-butanol; n-pentanol; n-hexanol; n-heptanol; n-
22 octanol; isooctanol; n-nonanol; n-decanol; n-dodecanol; n-
23 hexadecanol (cetyl alcohol); n-octadecanol (stearyl
24 alcohol); alcohols derived from linear C_{10} to C_{30} alpha
25 olefins and mixtures thereof; and alcohols derived from
26 polymers of C_2 to C_6 olefins, such as alcohols derived from
27 polypropylene and polybutene, including polypropylene
28 alcohols having 9 to about 30 carbon atoms. Particularly
29 preferred aliphatic alcohols are butanols.

30
31 The alkylphenols of formula VIII used in this invention may
32 be monoalkyl-substituted phenols or dialkyl-substituted
33 phenols. Monoalkyl-substituted phenols are preferred,
34 especially monoalkylphenols having an alkyl substituent in
35

01 the para position.

02

03 Preferably, the alkyl group of the alkylphenols employed in
04 this invention will contain 4 to about 24 carbon atoms, more
05 preferably 4 to 12 carbon atoms. Representative examples of
06 phenols suitable for use in this invention include, phenol,
07 methylphenol, dimethylphenol, ethylphenol, butylphenol,
08 octylphenol, decylphenol, dodecylphenol, tetradecylphenol,
09 hexadecylphenol, octadecylphenol, eicosylphenol,
10 tetracosylphenol, hexacosylphenol, triacontylphenol and the
11 like. Also, mixtures of alkylphenols may be employed, such
12 as a mixture of C_{14} - C_{18} alkylphenols, a mixture of C_{18} - C_{24}
13 alkylphenols, a mixture of C_{20} - C_{24} alkylphenols, or a mixture
14 of C_{16} - C_{26} alkylphenols.

15

16 Particularly preferred alkylphenols are those derived from
17 alkylation of phenol with polymers or oligomers of C_3 to C_6
18 olefins, such as polypropylene or polybutene. These
19 polymers preferably contain 10 to 30 carbon atoms. An
20 especially preferred alkylphenol is prepared by alkylating
21 phenol with a propylene polymer having an average of 4
22 units. This polymer has the common name of propylene
23 tetramer and is commercially available.

24

25 As indicated above, the poly(oxyalkylene) hydroxyaromatic
26 esters of formula III may be prepared by esterifying a
27 hydroxyaromatic carboxylic acid of formula IV with a
28 poly(oxyalkylene) alcohol of formula V under conventional
29 esterification reaction conditions.

30

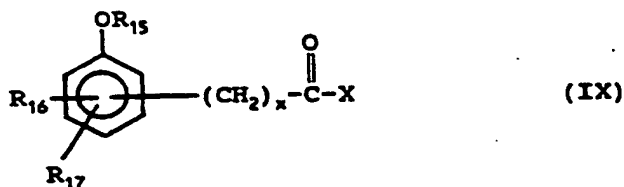
31 Typically, this reaction will be conducted by contacting a
32 poly(oxyalkylene) alcohol of formula V with about 0.25 to
33 about 1.5 molar equivalents of a hydroxyaromatic carboxylic
34 acid of formula IV in the presence of acidic catalyst at a

35

-17-

01 temperature in the range of 70°C to about 160°C for about
02 0.5 to about 48 hours. Suitable acid catalysts for this
03 reaction include p-toluenesulfonic acid, methanesulfonic
04 acid and the like. The reaction may be conducted in the
05 presence or absence of an inert solvent, such as benzene,
06 toluene and the like. The water generated by this reaction
07 is preferably removed during the course of the reaction by,
08 for example, azeotropic distillation with an inert solvent,
09 such as toluene.

10
11 The poly(oxyalkylene) hydroxyaromatic esters of formula III
12 may also be synthesized by reacting a poly(oxyalkylene)
13 alcohol of formula V with an acyl halide having the formula:



22 wherein X is a halide, such as chloride or bromide, and R_{15}
23 is a suitable hydroxyl protecting group, such as benzyl,
24 tert-butyldimethylsilyl, methoxymethyl, and the like; R_{16}
25 and R_{17} are each independently hydrogen, lower alkyl, lower
26 alkoxy, or the group $-\text{OR}_{18}$, wherein R_{18} is a suitable
27 hydroxyl protecting group.

28
29 Acyl halides of formula IX may be prepared from
30 hydroxyaromatic carboxylic acids of formula IV by first
31 protecting the aromatic hydroxyl groups of IV to form a
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01 carboxylic acid having the formula:

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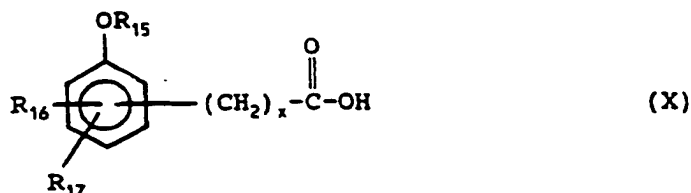
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wherein R_{15} - R_{17} and x are as defined above, and then converting the carboxylic acid moiety of X into an acyl halide using conventional procedures.

Protection of the aromatic hydroxyl groups of IV may be accomplished using well known procedures. The choice of a suitable protecting group for a particular hydroxyaromatic carboxylic acid will be apparent to those skilled in the art. Various protecting groups, and their introduction and removal, are described, for example, in T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, Second Edition, Wiley, New York, 1991, and references cited therein. Alternatively, the protected derivatives X can be prepared from known starting materials other than the hydroxyaromatic compounds of formula IV by conventional procedures.

The carboxylic acid moiety of X may be converted into an acyl halide by contacting X with an inorganic acid halide, such as thionyl chloride, phosphorous trichloride, phosphorous tribromide, or phosphorous pentachloride; or alternatively, with oxalyl chloride. Generally, this reaction will be conducted using about 1 to 5 molar equivalents of the inorganic acid halide or oxalyl chloride, either neat or in an inert solvent, such as diethyl ether, at a temperature in the range of about 20°C to about 80°C

-19-

01 for about 1 to about 48 hours. A catalyst, such as N,N-
02 dimethylformamide, may also be used in this reaction.

03

04 In certain cases where the hydroxyaromatic carboxylic acids
05 of formula IV having bulky alkyl groups adjacent to the
06 hydroxyl group, such as 3,5-di-t-butyl-4-hydroxybenzoic
07 acid, it will generally not be necessary to protect the
08 hydroxyl group prior to formation of the acyl halide, since
09 such hydroxyl groups are sufficiently sterically hindered so
10 as to be substantially non-reactive with the acyl halide
11 moiety.

12

13 Reaction of acyl halide IX with poly(oxyalkylene) alcohol V
14 provides an intermediate poly(oxyalkylene) ester having the
15 formula:

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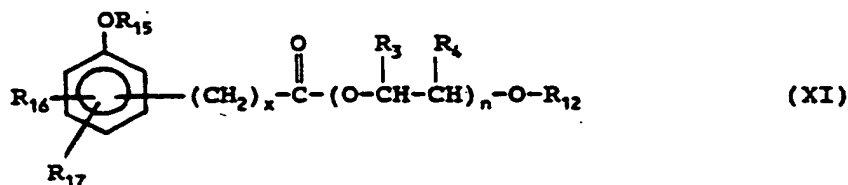
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wherein R_3 , R_4 , R_{12} , R_{15} - R_{17} , n and x are as defined above.

Typically, this reaction is conducted by contacting V with about 0.9 to about 1.5 molar equivalents of IX in an inert solvent, such as toluene, dichloromethane, diethyl ether, and the like, at a temperature in the range of about 25°C to about 150°C. The reaction is generally complete in about 0.5 to about 48 hours. Preferably, the reaction is conducted in the presence of a sufficient amount of an amine capable of neutralizing the acid generated during the reaction, such as triethylamine, di(isopropyl)ethylamine, pyridine or 4-dimethylamino-pyridine.

01 Deprotection of the aromatic hydroxyl group(s) of XI then
 02 provides a poly(oxyalkylene) hydroxyaromatic ester of
 03 formula III. Appropriate conditions for this deprotection
 04 step will depend upon the protecting group(s) utilized in
 05 the synthesis and will be readily apparent to those skilled
 06 in the art. For example, benzyl protecting groups may be
 07 removed by hydrogenolysis under 1 to about 4 atmospheres of
 08 hydrogen in the presence of a catalyst, such as palladium on
 09 carbon. Typically, this deprotection reaction is conducted
 10 in an inert solvent, preferably a mixture of ethyl acetate
 11 and acetic acid, at a temperature of from about 0°C to about
 12 40°C for about 1 to about 24 hours.

13

14 The poly(oxyalkylene) hydroxyaromatic esters of the present
 15 invention having the formula:

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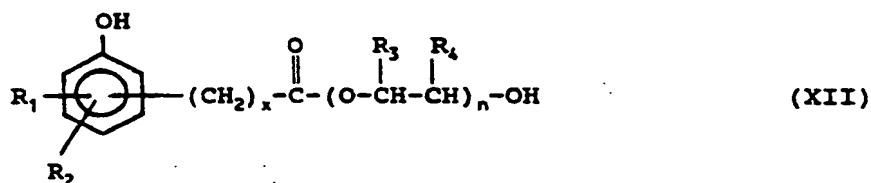
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wherein R_1 - R_4 , n and x are as defined above, can be prepared from compounds of formula III or XI, wherein $\text{R}_{1,2}$ is a benzyl group, by removing the benzyl group using conventional hydrogenolysis procedures. Compounds of formula III or XI where $\text{R}_{1,2}$ represents a benzyl group may be prepared by employing a metal salt VI derived from benzyl alcohol in the above described synthetic procedures.

-21-

01 Similarly, the poly(oxyalkylene) hydroxyaromatic esters of
 02 the present invention having the formula:

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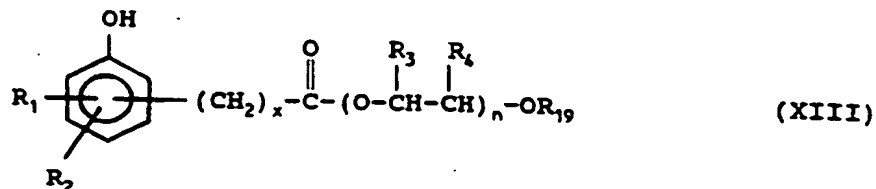
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11 wherein R_1 - R_4 , n and x are as defined above and R_{19} is an
 12 acyl group having the formula:

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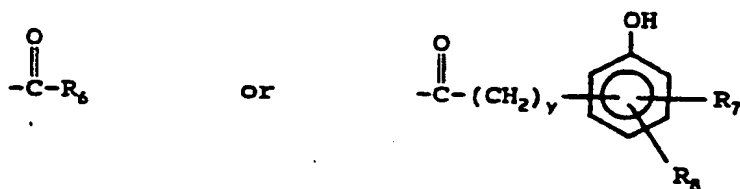
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20 wherein R_6 - R_8 and y are as defined above, can be synthesized
 21 in several steps from a compound of formula XI, wherein R_{12}
 22 represents a benzyl group and R_{15} (and optionally R_{18})
 23 represents a hydroxyl protecting group that is stable to
 24 hydrogenolysis conditions, such as a tert-butyldimethyl-
 25 silyl group. The synthesis of XIII from such compounds may
 26 be effected by first removing the benzyl group using
 27 conventional hydrogenolysis conditions and then acylating
 28 the resulting hydroxyl group with a suitable acylating
 29 agent. Removal of the protecting group(s) from the aromatic
 30 hydroxyl group(s) using conventional procedures then
 31 provides a poly(oxyalkylene) hydroxyaromatic ester of
 32 formula XIII.

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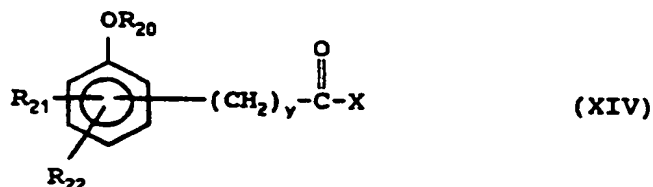
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Suitable acylating agents for use in this reaction include

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01 acyl halides, such as acyl chlorides and bromides; and
 02 carboxylic acid anhydrides. Preferred acylating agents are
 03 those having the formula: $R_6C(O)-X$, wherein R_6 is alkyl
 04 having 1 to 30 carbon atom, phenyl, or aralkyl or alkaryl
 05 having 7 to 36 carbon atoms, and X is chloro or bromo; and
 06 those having the formula:



16 wherein X is a halide, such as chloride or bromide, R_{20} is a
 17 suitable hydroxyl protecting group, R_{21} and R_{22} are each
 18 independently hydrogen, lower alkyl, lower alkoxy, or the
 19 group $-OR_{23}$, wherein R_{23} is a suitable hydroxyl protecting
 20 group, and y is an integer from 0 to 10.

21 A particularly preferred group of acylating agents are those
 22 having the formula: $R_{24}C(O)-X$, wherein R_{24} is alkyl having 4
 23 to 12 carbon atoms. Representative examples of such
 24 acylating agents include acetyl chloride, propionyl
 25 chloride, butanoyl chloride, pivaloyl chloride, octanoyl
 26 chloride, decanoyl chloride and the like.

27
 28
 29 Another particularly preferred group of acylating agents are
 30 those of formula XIV, wherein R_{20} is benzyl; R_{21} is hydrogen,
 31 alkyl having 1 to 4 carbon atoms, or $-OR_{25}$, wherein R_{25} is a
 32 suitable hydroxyl protecting group, preferably benzyl; R_{22}
 33 is hydrogen; and y is 0, 1 or 2. Representative examples of
 34 such acylating agents include 4-benzyloxybenzoyl chloride,
 35 3-benzyloxybenzoyl chloride, 4-benzyloxy-3-methylbenzoyl

-23-

01 chloride, 4-benzyloxyphenylacetyl chloride, 3-(4-
02 benzyloxyphenyl)propionyl chloride and the like.

03

04 Generally, this acylation reaction will be conducted using
05 about 0.95 to about 1.2 molar equivalents of the acylating
06 agent. The reaction is typically conducted in an inert
07 solvent, such as toluene, dichloromethane, diethyl ether and
08 the like, at a temperature in the range of about 25°C to
09 about 150°C for about 0.5 to about 48 hours. When an acyl
10 halide is employed as the acylating agent, the reaction is
11 preferably conducted in the presence of a sufficient amount
12 of an amine capable of neutralizing the acid generated
13 during the reaction, such as triethylamine, di(isopropyl)-
14 ethylamine, pyridine or 4-dimethylaminopyridine.

15

16 A particularly preferred group of poly(oxyalkylene)
17 hydroxyaromatic esters of formula XIII are those having the
18 same hydroxyaromatic ester group at each end the
19 poly(oxyalkylene) moiety, i.e. compounds of formula XIII
20 wherein R_1 is an acyl group having the formula:

21

22

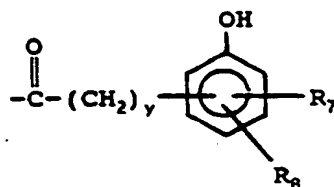
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29 wherein R_7 is the same group as R_1 , R_8 is the same group as
30 R_2 , and x and y are the same integer.

31

32 These compounds may be prepared from a poly(oxyalkylene)

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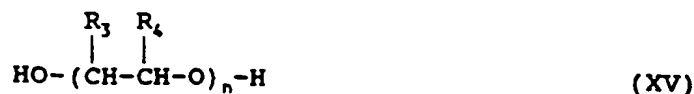
01 diol having the formula:

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Fuel Compositions

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wherein R_3 , R_4 , and n are as defined above, by esterifying each of the hydroxyl groups present in XV with a hydroxyaromatic carboxylic acid of formula IV or an acyl halide of formula IX using the above described synthetic procedures. The poly(oxyalkylene) diols of formula XV are commercially available or may be prepared by conventional procedures, for example, by using sodium or potassium hydroxide in place of the alkoxide or phenoxide metal salt VI in the above described alkylene oxide polymerization reaction.

The poly(oxyalkylene) hydroxyaromatic esters of the present invention are useful as additives in hydrocarbon fuels to prevent and control engine deposits, particularly intake valve deposits. The proper concentration of additive necessary to achieve the desired deposit control varies depending upon the type of fuel employed, the type of engine, and the presence of other fuel additives.

In general, the concentration of the poly(oxyalkylene) hydroxyaromatic esters of this invention in hydrocarbon fuel will range from about 50 to about 2500 parts per million (ppm) by weight, preferably from 75 to 1,000 ppm. When other deposit control additives are present, a lesser amount of the present additive may be used.

The poly(oxyalkylene) hydroxyaromatic esters of the present

01 invention may be formulated as a concentrate using an inert
02 stable oleophilic (i.e., dissolves in gasoline) organic
03 solvent boiling in the range of about 150°F to 400°F (about
04 65°C to 205°C). Preferably, an aliphatic or an aromatic
05 hydrocarbon solvent is used, such as benzene, toluene,
06 xylene or higher-boiling aromatics or aromatic thinners.
07 Aliphatic alcohols containing about 3 to 8 carbon atoms,
08 such as isopropanol, isobutylcarbinol, n-butanol and the
09 like, in combination with hydrocarbon solvents are also
10 suitable for use with the present additives. In the
11 concentrate, the amount of the additive will generally range
12 from about 10 to about 70 weight percent, preferably 10 to
13 50 weight percent, more preferably from 20 to 40 weight
14 percent.

15

16 In gasoline fuels, other fuel additives may be employed with
17 the additives of the present invention, including, for
18 example, oxygenates, such as t-butyl methyl ether, antiknock
19 agents, such as methylcyclopentadienyl manganese
20 tricarbonyl, and other dispersants/detergents, such as
21 hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, or
22 succinimides. Additionally, antioxidants, metal
23 deactivators and demulsifiers may be present.

24

25 In diesel fuels, other well-known additives can be employed,
26 such as pour point depressants, flow improvers, cetane
27 improvers, and the like.

28

29 A fuel-soluble, nonvolatile carrier fluid or oil may also be
30 used with the poly(oxyalkylene) hydroxyaromatic esters of
31 this invention. The carrier fluid is a chemically inert
32 hydrocarbon-soluble liquid vehicle which substantially
33 increases the nonvolatile residue (NVR), or solvent-free
34 liquid fraction of the fuel additive composition while not
35 overwhelmingly contributing to octane requirement increase.

-26-

01 The carrier fluid may be a natural or synthetic oil, such as
02 mineral oil, refined petroleum oils, synthetic polyalkanes
03 and alkenes, including hydrogenated and unhydrogenated
04 polyalphaolefins, and synthetic polyoxyalkylene-derived
05 oils, such as those described, for example, in U.S. Patent
06 No. 4,191,537 to Lewis.

07

08 These carrier fluids are believed to act as a carrier for
09 the fuel additives of the present invention and to assist in
10 removing and retarding deposits. The carrier fluid may also
11 exhibit synergistic deposit control properties when used in
12 combination with a hydroxyaromatic poly(oxyalkylene)
13 compound of this invention.

14

15 The carrier fluids are typically employed in amounts ranging
16 from about 100 to about 5000 ppm by weight of the
17 hydrocarbon fuel, preferably from 400 to 3000 ppm of the
18 fuel. Preferably, the ratio of carrier fluid to deposit
19 control additive will range from about 0.5:1 to about 10:1,
20 more preferably from 1:1 to 4:1, most preferably about 2:1.

21

22 When employed in a fuel concentrate, carrier fluids will
23 generally be present in amounts ranging from about 20 to
24 about 60 weight percent, preferably from 30 to 50 weight
25 percent.

26

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EXAMPLES

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29 The following examples are presented to illustrate specific
30 embodiments of the present invention and synthetic
31 preparations thereof; and should not be interpreted as
32 limitations upon the scope of the invention.

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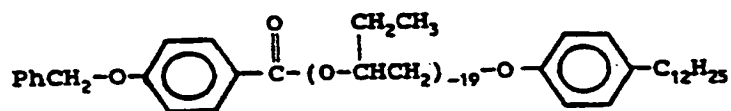
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Example 1Preparation of 4-Benzyloxybenzoyl Chloride

To a flask equipped with a magnetic stirrer and drying tube was added 10.0 grams of 4-benzyloxybenzoic acid and 100 mL of anhydrous diethyl ether and then 19.1 mL of oxalyl chloride. The resulting mixture was stirred at room temperature for 16 hours and then the solvent was removed in vacuo to yield 10.8 grams of the desired acid chloride.

Example 2Preparation of α -(4-Benzyloxybenzoyl)- ω -4-dodecylphenoxy poly(oxybutylene)

4-Benzyloxybenzoyl chloride (10.8 grams) from Example 1 was combined with 72.2 grams of α -hydroxy- ω -4-dodecylphenoxy poly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 150 mL of anhydrous toluene. Triethylamine (6.41 mL) and 4-dimethylaminopyridine (0.54 grams) were then added and the resulting mixture was heated to reflux under nitrogen for 16 hours. The reaction was then cooled to room temperature and diluted with 300 mL of diethyl ether. The organic layer was washed twice with 1% aqueous hydrochloric acid, twice with saturated aqueous sodium bicarbonate solution, and once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents

-28-

01 removed in vacuo to yield 76.5 grams of a light brown oil.
 02 The oil was chromatographed on silica gel, eluting with
 03 hexane/diethyl ether/ethanol (8:1.5:0.5), to yield 43.2
 04 grams of the desired product as a colorless oil.

05

06

Example 3

07

08

Preparation of

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 α -(4-Hydroxybenzoyl)- ω -4-dodecylphenoxypoly(oxybutylene)

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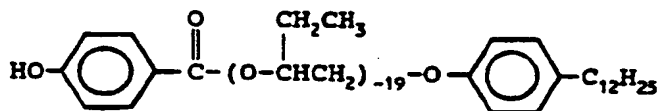
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A solution of 15.9 grams of the product from Example 2 in 50 mL of ethyl acetate and 50 mL of acetic acid containing 3.48 grams of 5% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of residual acetic acid with toluene in vacuo yielded 14.6 grams of the desired product as a colorless oil. The product had an average of 19 oxybutylene units. IR (neat) 1715 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.9, 7.3 (AB quartet, 4H), 7.1-7.25 (m, 2H), 6.7-6.9 (m, 2H), 5.05-5.15 (m, 1H), 3.1-4.0 (m, 56H), 0.5-1.9 (m, 120H).

Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

- α -(4-hydroxybenzoyl)- ω -n-butyloxypoly(oxybutylene);
- α -(4-hydroxybenzoyl)- ω -4-t-butylphenoxypoly(oxybutylene);
- α -(4-hydroxybenzoyl)- ω -4-octacosylphenoxypoly(oxybutylene);
- α -(4-hydroxy-3-methoxybenzoyl)- ω -4-dodecylphenoxy-

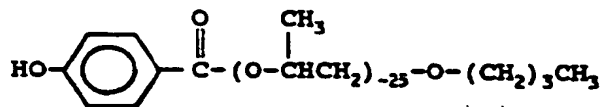
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01 poly(oxybutylene);
 02 α -(4-hydroxy-3-methylbenzoyl)- ω -4-dodecylphenoxy-
 03 poly(oxybutylene); and
 04 α -(3,4-dihydroxybenzoyl)- ω -4-dodecylphenoxy-
 05 poly(oxybutylene).
 06

07 Example 4

08 Preparation of

09 α -(4-Hydroxybenzoyl)- ω -n-butoxypoly(oxypropylene)



15

16 To a flask equipped with a magnetic stirrer, thermometer,
 17 Dean-Stark trap, nitrogen inlet and reflux condenser was
 18 added 4.52 grams of 4-hydroxybenzoic acid, 50.0 grams of α -
 19 hydroxy- ω -n-butoxypoly(oxypropylene) having an average of 25
 20 oxypropylene units (commercially available from Union
 21 Carbide as LB385) and 0.56 grams of p-toluenesulfonic acid.
 22 The reaction was heated to 120°C for 16 hours and then
 23 cooled to room temperature. Diethyl ether (750 mL) was
 24 added and the organic phase was washed twice with saturated
 25 aqueous sodium bicarbonate, and once with saturate aqueous
 26 sodium chloride solution. The organic layer was then dried
 27 over anhydrous magnesium sulfate, filtered and concentrated
 28 in vacuo to afford 51.7 grams of a brown oil. The oil was
 29 chromatographed on silica gel, eluting with hexane/ethyl
 30 acetate/ethanol (49:49:2) to yield 25.2 grams of the desired
 31 product as a yellow oil. The product had an average of 25
 32 oxypropylene units. IR (neat) 1715 cm^{-1} ; ^1H NMR (CDCl_3) δ
 33 7.9, 6.85 (AB quartet, 4H), 5.05-5.15 (m, 1H), 3.1-4.0 (m,
 34 76H), 1.4-1.6 (m, 2H), 1.25-1.4 (m, 2H), 0.9-1.4 (m, 75H),
 35

-30-

01 0.75-0.9 (t, 3H).

02

03 Similarly, by using the above procedures and the appropriate
04 starting materials and reagents, the following compounds can
05 be prepared:

06

07 α -(4-hydroxybenzoyl)- ω -4-t-butylphenoxypoly(oxypropylene);

08 α -(4-hydroxybenzoyl)- ω -4-dodecylphenoxypoly(oxypropylene);

09 α -(4-hydroxy-3-methoxybenzoyl)- ω -n-butoxypoly(oxypropylene);

10 α -(4-hydroxy-3-methylbenzoyl)- ω -n-butoxypoly(oxypropylene);

11 and

12 α -(3,4-dihydroxybenzoyl)- ω -n-butoxypoly(oxybutylene).

13

14 Example 5

15

16 Preparation of 2-Benzoyloxybenzoyl Chloride

17

18 To a flask equipped with a magnetic stirrer and drying tube
19 was added 15.0 grams of 2-benzoyloxybenzoic acid and 150 mL
20 of anhydrous dichloromethane followed by 28.7 mL of oxalyl
21 chloride. The reaction was stirred at room temperature for
22 16 hours, and then the solvent was removed in vacuo to yield
23 16.2 grams of the desired acid chloride.

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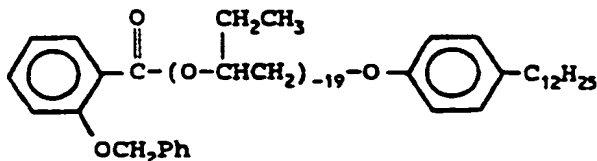
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Example 6

Preparation of

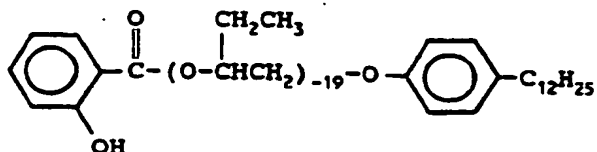
 α -(2-Benzoyloxybenzoyl)- ω -4-dodecylphenoxypoly(oxybutylene)

2-Benzoyloxybenzoyl chloride (16.2 grams) from Example 5 was combined with 108.3 grams of α -hydroxy- ω -4-dodecylphenoxy-poly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 225 mL of anhydrous toluene. Triethylamine (9.6 mL) and 4-dimethylaminopyridine (0.8 grams) were added and the reaction was heated to reflux under nitrogen for 16 hours, then cooled to room temperature and diluted with 500 mL of diethyl ether. The organic layer was washed twice with 1% aqueous hydrochloric acid, twice with saturated aqueous sodium bicarbonate solution, and once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to yield 119.2 grams of a light brown oil. The oil was chromatographed on silica gel, eluting with hexane/diethyl ether/ethanol (8:1.5:0.5) to yield 73.0 grams of the desired product as a light brown oil.

-32-

Example 7

Preparation of

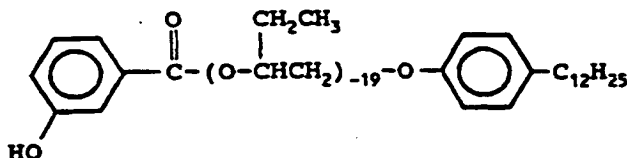
 α -(2-Hydroxybenzoyl)- ω -4-dodecylphenoxy poly(oxybutylene)

A solution of 30.8 grams of the product from Example 6 in 95 mL of ethyl acetate and 95 mL of acetic acid containing 3.39 grams of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of solvent in vacuo followed by azeotropic removal of residual acetic acid with toluene under vacuum yielded 28.9 grams of the desired product as a light brown oil. The product had an average of 19 oxybutylene units. IR (neat) 1673 cm⁻¹, ¹H NMR (CDCl₃) δ 10.85 (s, 1H), 7.8-8.2 (m, 8H), 5.1-5.3 (m, 1H), 3.2-4.1 (m, 56H), 0.5-1.9 (m, 21H).

-33-

Example 8

Preparation of

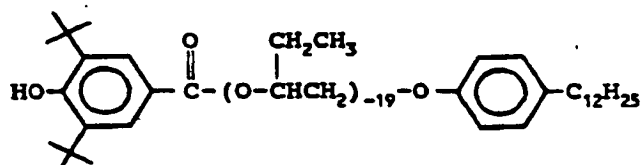
 α -(3-Hydroxybenzoyl)- ω -4-dodecylphenoxy poly(oxybutylene)

To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, nitrogen inlet and reflux condenser was added 5.08 grams of 3-hydroxybenzoic acid, 50.0 grams of α -hydroxy- ω -4-dodecylphenoxy-poly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 0.53 grams of p-toluenesulfonic acid. The reaction was heated to 130°C for 48 hours and then cooled to room temperature. Diethyl ether (750 mL) was added and the organic phase was washed twice with saturated aqueous sodium bicarbonate and once with saturated aqueous sodium chloride solution. The organic layer was then dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to afford 47.8 grams of a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate/ethanol (78:20:2) to yield 16.5 grams of the desired product as a yellow oil. The product had an average of 19 oxybutylene groups. IR (neat) 1716 cm^{-1} ; 1H NMR ($CDCl_3$) δ 6.6-7.6 (m, 8H), 4.9-5.2 (m, 1H), 3.1-4.0 (m, 56H), 0.5-1.9 (m, 21H).

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Example 9Preparation of 3,5-Di-t-butyl-4-hydroxybenzoyl Chloride

To a flask equipped with a magnetic stirrer, reflux condenser and nitrogen inlet was added 1.88 grams of 3,5-di-t-butyl-4-hydroxybenzoic acid and 15 mL of thionyl chloride. The reaction was refluxed for 2 hours and stirred at room temperature for 16 hours. The excess thionyl chloride was removed in vacuo to yield 2.2 grams of the desired acid chloride as a white solid.

Example 10Preparation of α -(3,5-Di-t-butyl-4-hydroxybenzoyl)-
 ω -4-dodecylphenoxypoly(oxybutylene)

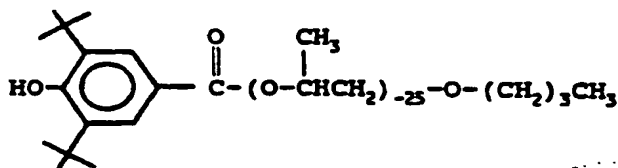
3,5-Di-t-butyl-4-hydroxybenzoyl chloride (2.2 grams) from Example 9 was combined with 13.6 grams of α -hydroxy- ω -4-dodecylphenoxy-poly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 50 mL of anhydrous toluene. Triethylamine (1.17 mL) and 4-dimethylaminopyridine (0.1 grams) were added and the reaction was heated to reflux under nitrogen for 16 hours, and then cooled to room temperature and diluted with 100 mL of hexane. The organic layer was washed twice with water, once with saturated aqueous sodium bicarbonate solution and once with saturated aqueous sodium chloride. The organic

-35-

01 layer was dried over anhydrous magnesium sulfate, filtered
02 and concentrated in vacuo to give an oil. The oil was
03 chromatographed on silica gel, eluting with hexane/diethyl
04 ether/ethanol (6:3.5:0.5) to yield 3.0 grams of the desired
05 product as a yellow oil. IR (neat) 1715 cm^{-1} ; ^1H NMR (CDCl_3)
06 δ 7.8 (s, 2H), 7.1-7.25 (m, 2H), 6.7-6.9 (m, 2H), 5.7 (s,
07 1H), 7.1-7.25 (m, 2H), 6.7-6.9 (m, 2H), 5.7 (s, 1H), 5.05-
08 5.15 (m, 1H), 3.1-4.0 (m, 56H), 0.5-1.9 (m, 138H).

10 Example 11

11
12 Preparation of α -(3,5-Di-*t*-butyl-4-hydroxybenzoyl)-
13 ω -*n*-butoxypoly(oxypropylene)



21 3,5-Di-*t*-butyl-4-hydroxybenzoyl chloride (8.0 grams)
22 prepared as described in Example 9 was combined with 46.2
23 grams of α -hydroxy- ω -*n*-butoxypoly(oxypropylene) having an
24 average of 25 oxypropylene units (commercially available
25 from Union Carbide as LB385) and 200 mL of anhydrous
26 toluene. Triethylamine (4.4 mL) and 4-dimethylaminopyridine
27 (0.37 grams) were added and the reaction was heated to
28 reflux under nitrogen for 16 hours, and then cooled to room
29 temperature and diluted with 500 mL of hexane. The organic
30 layer was washed twice with water, once with saturated
31 aqueous sodium bicarbonate solution and once with saturated
32 aqueous sodium chloride. The organic layer was dried over
33 anhydrous magnesium sulfate, filtered and concentrated in
34 vacuo to give an oil. The oil was chromatographed on silica
35 gel, eluting with hexane/diethyl ether/ethanol (6:3.5:0.5)

-36-

01 to yield 42.0 grams of the desired product as a yellow oil.
02 The product had an average of 25 oxypropylene units. IR
03 (neat) 1715 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.8 (s, 2H), 5.7 (s, 1H),
04 5.05-5.15 (m, 1H), 3.2-3.9 (m, 75H), 0.9-1.6 (m, 97H), 0.75-
05 0.9 (t, 3H).

06

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Example 12

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09

Preparation of α -[(4-Hydroxyphenyl)acetyl]-
10 ω -4-dodecylphenoxypoly(oxybutylene)

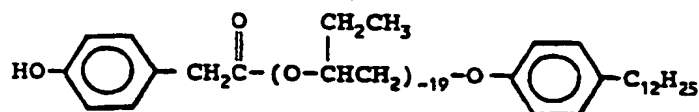
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To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, nitrogen inlet and reflux condenser was added 4.66 grams of 4-hydroxyphenylacetic acid, 50.0 grams of α -hydroxy- ω -4-dodecylphenoxypoly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 0.63 grams of p-toluenesulfonic acid. The reaction was heated to 120°C for 16 hours and then cooled to room temperature. Diethyl ether (750 mL) was added and the organic phase was washed twice with saturated aqueous sodium bicarbonate, and then once with saturated aqueous sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to afford 51.6 grams of a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate/ethanol (93:5:2) to yield 26.2 grams of the desired product as a yellow oil. The product had an average of 19 oxybutylene units. IR (neat) 1742 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.7-7.25 (m, 8H), 4.8-5.0 (m, 1H), 3.1-4.05 (m, 58H), 0.5-

01 1.9 (m, 120H).

02

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Example 13

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05 Preparation of α -[3-(4-Hydroxyphenyl)propionyl]-
06 ω -4-dodecylphenoxypoly(oxybutylene)

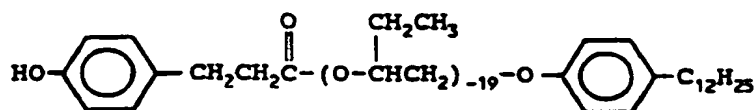
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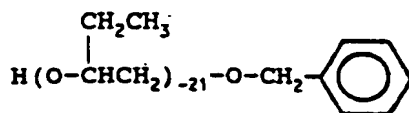
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To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, nitrogen inlet and reflux condenser was added 5.09 grams of 3-(4-hydroxyphenyl)propionic acid, 50.0 grams of α -hydroxy- ω -4-dodecylphenoxypoly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 0.63 grams of p-toluenesulfonic acid. The reaction was heated to 120°C for 16 hours and then cooled to room temperature. Diethyl ether (750 mL) was added and the organic phase was washed twice with saturated aqueous sodium bicarbonate, and once with saturated aqueous sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to afford 52.7 grams of a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate/ethanol (93:5:2) to yield 37.5 grams of the desired product as a yellow oil. IR (neat) 1735 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.7-7.25 (m, 8H), 4.8-5.0 (m, 1H), 3.1-4.05 (m, 56H), 2.9 (t, 2H), 2.55 (t, 2H), 0.5-0.9 (m, 120H).

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Example 14

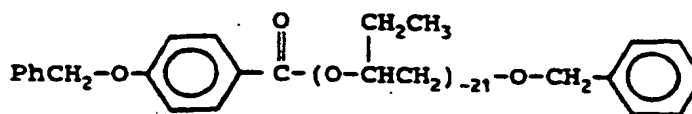
Preparation of α -Benzylloxy- ω -4-hydroxypoly(oxybutylene)

To a flask equipped with a mechanical stirrer, thermometer, addition funnel, reflux condenser and nitrogen inlet was added 1.59 grams of a 35 wt.% dispersion of potassium hydride in mineral oil. Benzyl alcohol (5.0 grams) dissolved in 250 mL of anhydrous toluene was added dropwise. After hydrogen evolution had subsided, the reaction was heated to reflux for 3 hours and then cooled to room temperature. 1,2-Epoxybutane (99.6 mL) were then added dropwise and the reaction was refluxed for 16 hours. The reaction was cooled to room temperature, quenched with 5 mL of methanol and diluted with 500 mL of diethyl ether. The resulting mixture was washed with saturated aqueous ammonium chloride, followed by water and saturated aqueous sodium chloride. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 64.1 grams of a yellow oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate/ethanol (90:8:2) to afford 40 grams of the desired product as a light yellow oil.

-39-

Example 15

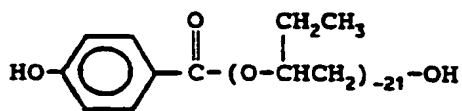
Preparation of

 α -(4-Benzoyloxybenzoyl)- ω -benzyloxypoly(oxybutylene)

4-Benzoyloxybenzoyl chloride (10.8 grams) from Example 1 was combined with α -benzyloxy- ω -hydroxy-poly(oxybutylene) (15.0 grams) from Example 14 and 50 mL of anhydrous toluene. Triethylamine (1.3 mL) and 4-dimethylaminopyridine (0.55 grams) were then added and the resulting mixture was heated to reflux under nitrogen for 16 hours. The reaction was then cooled to room temperature and diluted with 100 mL of diethyl ether. The organic layer was washed twice with 1% aqueous hydrochloric acid, twice with saturated aqueous sodium bicarbonate solution, and once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 16.8 grams of the desired product as a yellow oil.

Example 16

Preparation of

 α -(4-Hydroxybenzoyl)- ω -hydroxypoly(oxybutylene)

A solution of 16.8 grams of the product from Example 15 in

-40-

01 100 mL of ethyl acetate and 100 mL of acetic acid containing
02 3.0 grams of 5% palladium on charcoal was hydrogenolyzed at
03 35-40 psi for 16 hours on a Parr low-pressure hydrogenator.
04 Catalyst filtration and removal of residual acetic acid with
05 toluene in vacuo yielded 14.8 grams of the desired product
06 as a yellow oil. The product had an average of 21
07 oxybutylene units. IR (neat) 1715 cm^{-1} ; ^1H NMR (CDCl_3) δ
08 7.9, 6.8 (AB quartet, 4H), 5.05-5.15 (m, 1H), 3.1-3.9 (m,
09 62H), 0.6-1.9 (m, 105H).

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Comparative Example A

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Preparation of Polyisobutylphenol

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15 To a flask equipped with a magnetic stirrer, reflux
16 condenser, thermometer, addition funnel and nitrogen inlet
17 was added 203.2 grams of phenol. The phenol was warmed to
18 40°C and boron trifluoride etherate (73.5 mL) was added
19 dropwise. Ultravis 10 polyisobutene (1040 grams, molecular
20 weight 950, 76% methylvinylidene isomer, available from
21 British Petroleum), dissolved in 1,863 mL of hexane, was
22 then added to the reaction mixture at a rate sufficient to
23 maintain the temperature between 22-27°C. The reaction
24 mixture was then stirred for 16 hours at room temperature.
25 Concentrated ammonium hydroxide (400 mL) was then added and
26 the mixture was diluted with 2 L of hexane. The resulting
27 mixture was washed with water (3 x 2 L), dried over
28 anhydrous magnesium sulfate, filtered and the solvent
29 removed in vacuo to yield 1,056.5 grams of an oil. This oil
30 was determined to contain 80% of the desired
31 polyisobutenylphenol and 20% polyisobutene by ^1H NMR and
32 also by chromatography on silica gel, eluting first with
33 hexane and then with hexane/ethyl acetate/ethanol (93:5:2).

34

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Example 17

02

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Single-Cylinder Engine Test

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05 The test compounds were blended in gasoline and their
06 deposit reducing capacity determined in an ASTM/CFR single-
07 cylinder engine test.

08

09 A Waukesha CFR single-cylinder engine was used. Each run
10 was carried out for 15 hours, at the end of which time the
11 intake valve was removed, washed with hexane and weighed.
12 The previously determined weight of the clean valve was
13 subtracted from the weight of the valve at the end of the
14 run. The differences between the two weights is the weight
15 of the deposit. A lesser amount of deposit indicates a
16 superior additive. The operating conditions of the test
17 were as follows: water jacket temperature 200°F; vacuum of
18 12 in Hg, air-fuel ratio of 12, ignition spark timing of 40°
19 BTC; engine speed is 1800 rpm; the crankcase oil is a
20 commercial 30W oil.

21

22 The amount of carbonaceous deposit in milligrams on the
23 intake valves is reported for each of the test compounds in
24 Table I.

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TABLE I

Intake Valve Deposit Weight (in milligrams)			
Sample ¹	Run 1	Run 2	Average
Base Fuel	214.7	193.7	204.2
Example 3	7.1	9.1	8.1
Example 4	127.7	128.4	128.1
Example 7	150.0	215.4	182.7
Example 8	62.3	57.5	59.9
Example 10	108.0	95.1	101.6
Example 11	117.1	124.6	120.9
Example 12	84.6	98.4	91.5
Example 13	90.5	90.7	90.6
Example 16	41.1	43.0	42.1

¹ At 200 parts per million actives (ppma).

The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 200 ppma (parts per million actives).

The data in Table I illustrates the significant reduction in intake valve deposits provided by the poly(oxyalkylene) hydroxyaromatic esters of the present invention (Examples 3, 4, 7, 8, 10, 11, 12, 16) compared to the base fuel.

01

Example 18

02

03

Multicylinder Engine Test

04

05 The poly(oxyalkylene) hydroxyaromatic esters of the present
06 invention were tested in a laboratory multicylinder engine
07 to evaluate their intake valve and combustion chamber
08 deposit control performance. The test engine was a 4.3
09 liter, TBI (throttle body injected), V6 engine manufactured
10 by General Motors Corporation.

11

12 The major engine dimensions are set forth in Table II:

13

Table II

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Engine Dimensions

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Bore	10.16 cm
Stroke	8.84 cm
Displacement Volume	4.3 liter
Compression Ratio	9.3:1

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The test engine was operated for 40 hours (24 hours a day)
on a prescribed load and speed schedule representative of
typical driving conditions. The cycle for engine operation
during the test is set forth in Table III.

-44-

Table III

Engine Driving Cycle

Step	Mode	Time in Mode, [Sec]	Dynamometer Load [kg]	Engine Speed [RPM]
1	Idle	60	0	800
2	City Cruise	150	10	1,500
3	Acceleration	40	25	2,800
4	Heavy HWY Cruise	210	15	2,200
5	Light HWY Cruise	60	10	2,200
6	Idle	60	0	800
7	City Cruise	180	10	1,500
8	Idle	60	0	800

¹ All steps, except step number 3, include a 15 second transition ramp. Step 3 includes a 20 second transition ramp.

All of the test runs were made with the same base gasoline, which was representative of commercial unleaded fuel. The results are set forth in Table IV.

Table IV

Multicylinder Engine Test Results

Sample ¹		Intake Valve Deposits ²	Combustion Chamber Deposits ²
Base Fuel	Run 1	951	1887
	Run 2	993	1916
	Average	972	1902
Example 3	Run 1	48	2173
	Run 2	48	2205
	Average	48	2189
Comparative	Run 1	229	2699
Example A	Run 2	218	2738
	Average	224	2719

¹ At 400 parts per million actives (ppma).

² In milligrams (mg).

The base fuel employed in the above multicylinder engine tests contained no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 400 ppma (parts per million actives).

The data in Table IV illustrates the significant reduction in intake valve deposits provided by the poly(oxyalkylene) hydroxyaromatic esters of the present invention (Example 3) compared to the base fuel. Moreover, the data in Table IV further demonstrates the significant reduction in combustion chamber deposits produced by the poly(oxyalkylene) hydroxyaromatic ethers of the present invention (Example 3) compared to a known polyisobutylphenol fuel additive (Comparative Example A).

01 WHAT IS CLAIMED IS:

02

03 1. A compound of the formula:

04

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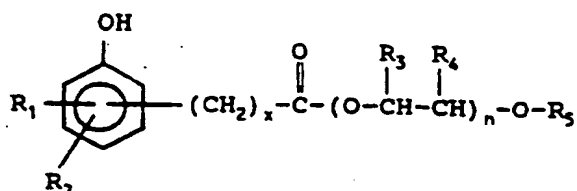
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or a fuel-soluble salt thereof; wherein

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R_1 and R_2 are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

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R_3 and R_4 are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

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23

R_5 is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group having the formula:

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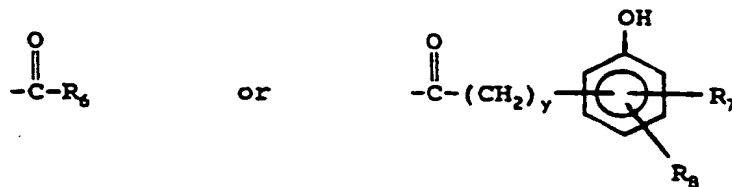
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wherein R_6 is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms; R_7 and R_8 are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

-47-

- 01 n is an integer from 5 to 100; and x and y are each
02 independently an integer from 0 to 10.
03
- 04 2. The compound according to Claim 1, wherein n is an
05 integer ranging from 10 to 50.
06
- 07 3. The compound according to Claim 2, wherein n is an
08 integer ranging from 15 to 30.
09
- 10 4. The compound according to Claim 2, wherein R₁ is
11 hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon
12 atoms; and R₂ is hydrogen.
13
- 14 5. The compound according to Claim 4, wherein R₃ is
15 hydrogen, alkyl having 2 to 22 carbon atoms, or
16 alkylphenyl having an alkyl group containing 4 to 24
17 carbon atoms.
18
- 19 6. The compound according to Claim 5, wherein R₁ is
20 hydrogen or hydroxy.
21
- 22 7. The compound according to Claim 6, wherein R₃ is
23 hydrogen, alkyl having 4 to 12 carbon atoms, or
24 alkylphenyl having an alkyl group containing 4 to 12
25 carbon atoms.
26
- 27 8. The compound according to Claim 7, wherein one of R₃
28 and R₄ is lower alkyl having 1 to 3 carbon atoms and
29 the other is hydrogen.
30
- 31 9. The compound according to Claim 8, wherein one of R₃
32 and R₄ is methyl or ethyl and the other is hydrogen.
33
- 34 10. The compound according to Claim 9, wherein x is 0, 1 or
35 2.

01

02 11. The compound according to Claim 10, wherein R_1 is
 03 hydrogen, R_2 is alkylphenyl having an alkyl group
 04 containing 4 to 12 carbon atoms, and x is 0.

05

06 12. A fuel composition comprising a major amount of
 07 hydrocarbons boiling in the gasoline or diesel range
 08 and an effective detergent amount of a compound of the
 09 formula:

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or a fuel-soluble salt thereof; wherein

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R_1 and R_2 are each independently hydrogen, hydroxy,
 lower alkyl having 1 to 6 carbon atoms, or lower alkoxy
 having 1 to 6 carbon atoms;

23

24

25

R_3 and R_4 are each independently hydrogen or lower
 alkyl having 1 to 6 carbon atoms;

26

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R_5 is hydrogen, alkyl having 1 to 30 carbon atoms,
 phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms,
 or an acyl group of the formula:

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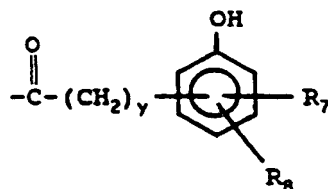
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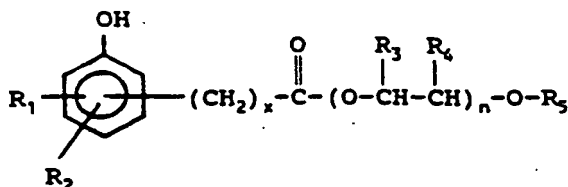


or



- 01
02 wherein R_6 is alkyl having 1 to 30 carbon atoms,
03 phenyl, or aralkyl or alkaryl having 7 to 36 carbon
04 atoms; R_7 and R_8 are each independently hydrogen,
05 hydroxy, lower alkyl having 1 to 6 carbon atoms, or
06 lower alkoxy having 1 to 6 carbon atoms;
07
08 n is an integer from 5 to 100; and x and y are each
09 independently an integer from 0 to 10.
10
- 11 13. The fuel composition according to Claim 12, wherein R_1
12 is hydrogen, hydroxy, or lower alkyl having 1 to 4
13 carbon atoms; R_2 is hydrogen; one of R_3 and R_4 is
14 hydrogen and the other is methyl or ethyl; R_5 is
15 hydrogen, alkyl having 2 to 22 carbon atoms, or
16 alkylphenyl having an alkyl group containing 4 to 24
17 carbon atoms; n is 15 to 30 and x is 0, 1 or 2.
18
- 19 14. The fuel composition according to Claim 13, wherein R_1
20 is hydrogen or hydroxy; R_2 is hydrogen, alkyl having 4
21 to 12 carbon atoms, or alkylphenyl having an alkyl
22 group containing 4 to 12 carbon atoms; and x is 0.
23
- 24 15. The fuel composition according to Claim 14, wherein R_1
25 is hydrogen, and R_2 is alkylphenyl having an alkyl
26 group containing 4 to 12 carbon atoms.
27
- 28 16. The fuel composition according to Claim 12, wherein
29 said composition contains about 50 to about 2500 parts
30 per million by weight of said compound.
31
32
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- 01 17. A fuel concentrate comprising an inert stable
 02 oleophilic organic solvent boiling in the range of from
 03 about 150°F to 400°F and from about 10 to about 70
 04 weight percent of a compound of the formula:

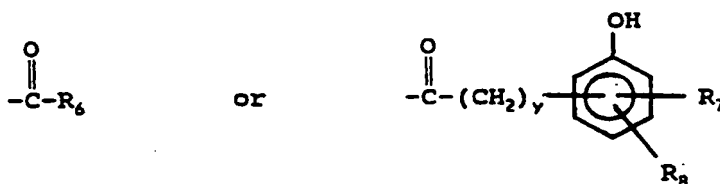


13 or a fuel-soluble salt thereof; wherein

14
 15 R₁ and R₂ are each independently hydrogen, hydroxy,
 16 lower alkyl having 1 to 6 carbon atoms, or lower alkoxy
 17 having 1 to 6 carbon atoms;

18
 19 R₃ and R₄ are each independently hydrogen or lower
 20 alkyl having 1 to 6 carbon atoms;

21
 22 R₅ is hydrogen, alkyl having 1 to 30 carbon atoms,
 23 phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms,
 24 or an acyl group of the formula:



33 wherein R₆ is alkyl having 1 to 30 carbon atoms,
 34 phenyl, or aralkyl or alkaryl having 7 to 36 carbon
 35 atoms; R₇ and R₈ are each independently hydrogen,

- 01 hydroxy, lower alkyl having 1 to 6 carbon atoms, or
02 lower alkoxy having 1 to 6 carbon atoms;
03
04 n is an integer from 5 to 100; and x and y are each
05 independently an integer from 0 to 10.
06
- 07 18. The fuel concentrate according to Claim 17, wherein R₁
08 is hydrogen, hydroxy, or lower alkyl having 1 to 4
09 carbon atoms; R₂ is hydrogen; one of R₃ and R₄ is
10 hydrogen and the other is methyl or ethyl; R₅ is
11 hydrogen, alkyl having 2 to 22 carbon atoms, or
12 alkylphenyl having an alkyl group containing 4 to 24
13 carbon atoms; n is 15 to 30 and x is 0, 1 or 2.
14
- 15 19. The fuel concentrate according to Claim 18, wherein R₁
16 is hydrogen or hydroxy; R₂ is hydrogen, alkyl having 4
17 to 12 carbon atoms, or alkylphenyl having an alkyl
18 group containing 4 to 12 carbon atoms; and x is 0.
19
- 20 20. The fuel concentrate according to Claim 19, wherein R₁
21 is hydrogen, and R₂ is alkylphenyl having an alkyl
22 group containing 4 to 12 carbon atoms.
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/12361

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C10L 1/18; C07C 69/76

US CL : 44/389, 400; 560/61, 63

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/385,386387,388,389,400; 560/60, 61, 103

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Chemical Abstracts: structure search

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,245,030 (Faust et al) 13 January 1981, see abstract and claims.	1-11
X	US,A, 3,944,594 (Kleiner et al) 16 March 1976, see entire document.	1-20
A	US,A, 3,758,282 (Owen et al) 11 September 1973, see entire document.	1-20
A	US,A, 2,937,933 (Heisler et al) 24 May 1960, see entire document.	1-20

☐

Further documents are listed in the continuation of Box C.

☐

See patent family annex.

- * Special categories of cited documents:
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Date of the actual completion of the international search

13 MAY 1994

Date of mailing of the international search report

MAY 31 1994

Name and mailing address of the ISA/US
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